Physical Basis for Hund's Rule

N. Karayianis and C. A. Morrison

Harry Diamond Laboratories, Washington, D. C. 20025

It is shown that a consideration of the Coulombic and spin–orbit interactions between the electrons of a given atomic configuration is sufficient to arrive at a lowest-energy state consistent with Hund's rule. The maximum-spin requirement of Hund's rule is a result of minimum Coulombic energy alone, whereas maximum orbital angular momentum consistent with maximum spin is a result of minimum spin–orbit energy. It is argued that, to first order, the spin–spin interaction is not a principal factor in determining the properties of this state. The simple notions used to obtain these results are extended to excited states of the nf^6 configuration and are shown to give results consistent with calculations based on hydrogenic wavefunctions.

I. INTRODUCTION

THE empirical rule for determining the lowest-lying level of a given atomic configuration was discovered by Hund in 1925 and today bears his name.[1-5] The rule is usually stated as follows: For a given atomic configuration, an energy level with largest total spin S lies deepest and, of these, the level with largest total orbital angular momentum L lies deepest. In his book published in 1927,[6] Hund states an additional rule that applies only to configurations of equivalent electrons.[7] This rule may be stated as follows: Where the number of equivalent electrons N is less than or equal to half a filled shell, the total angular momentum J of the deepest level is given by $J = |L - S|$ and, otherwise, by $J = L + S$.[8]

Without going too far afield, it is safe to say that Hund's rule is found to hold with but one known exception[9] for ground configurations of all atoms. In those atoms (primarily those with large atomic number) where there is a breakdown

of Russel–Saunders (LS) coupling, the rule must be interpreted as determining the state to which the physical ground state would tend in the limit of vanishing spin–orbit coupling.

The purpose of this paper is to present certain physical arguments that lead to an understanding of the observed validity of Hund's rule. The arguments are presented specifically for configurations involving equivalent electrons, as their application to other configurations is straightforward.

To demonstrate the use of Hund's rule, let us consider the atomic configuration nd^2; that is, outside of closed shells there are two electrons, each[10] with principal quantum number n, and orbital angular-momentum quantum number $l = 2$ (hence equivalent).[11] The maximum total spin S is obtained by assigning to each electron the maximum spin projection $m_s = \frac{1}{2}$, hence $S = 1$ in this case.[12] With this assignment the electrons possess identical n, l, and m_s quantum numbers. Pauli's exclusion principle thus requires the projections of $1(m_l)$ to be different so that the maximum orbital angular momentum possible[12] is $L = 3$. Further, since we are considering two electrons in a shell which can accommodate ten,

[1] F. Hund, Z. Physik, **33**, 345 (1925).
[2] F. Hund, Z. Physik, **34**, 296 (1925).
[3] F. Hund, *Linienspektren und Periodisches System der Elemente* (Verlag-Julius Springer, Berlin, 1927), p. 124.
[4] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (University Press, Cambridge, New York, 1959), p. 209.
[5] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), 1st ed., p. 194.
[6] See Ref. 3., p. 126.
[7] Atomic electrons are equivalent if they share single-electron states that have the same principal and orbital angular-momentum quantum numbers, or, in other words, electrons in the same shell.
[8] In the jargon of spectroscopists, the former is said to be a normal fine structure whereas the latter is called inverted.
[9] W. C. Martin, Jr., J. Opt. Soc. Am. **53**, 1047 (1963).

[10] Throughout the paper, reference is made to individual electrons in order to economize on words. The reader should interpret "electron(s)" to mean "single electron state(s)." Because of the indistinguishability of the electrons, they share all of the distinct single-electron states to which definite quantum numbers can be assigned.
[11] This configuration is exhibited by neutral Zirconium and Hafnium, for example.
[12] Actually what is maximized is the projection of the total spin (orbital angular momentum) $M_S(M_L)$ taken along some direction, say the z axis. Those familiar with angular-momentum states recognize that this maximum is equal to the total-spin (orbital angular-momentum) quantum number $S(L)$.

the rule states that the total angular momentum is given by $J = L - S = 2$. The atomic system described by the quantum numbers $S = 1$, $L = 3$, and $J = 2$ is designated $^3F_2$. If the two d electrons are not equivalent, i.e., in the configuration $ndn'd$ where $n' \neq n$, then the projections m_l need not differ and $L = 4$ is possible. Hund's rule does not provide the value for J in this case,[13] and the state is designated simply by ^3G.

In Sec. II, the physical arguments leading to a ground state consistent with Hund's rule are presented. In Sec. III, these arguments are shown to give correct results even when applied to excited states of the nf^6 configuration, whereas a natural extension of Hund's rule fails.

II. LOWEST LEVEL

One method for handling the energy $E(\mathbf{r})$ due to the electrostatic repulsion between electrons in an atom is to introduce a fictitious potential energy $U_i(r)$ into the Hamiltonian for the system.[14,15] This potential energy is adjusted to describe the major portion of the true interaction so that $E(\mathbf{r}) - U(r)$ is small and may be treated by ordinary perturbation methods. Although this procedure is useful for obtaining quantitative results, the importance of the electrostatic energy relative to the spin–orbit and spin–spin energies is not clear when assessed from such a perspective. For our purposes, it is necessary to consider these interactions before any averaging.

An accurate, rigorous appraisal of the magnitudes of the electronic interactions in a given configuration requires machinery far too complicated to provide a simple physical picture of the situation. Let us then simply assume that the electrostatic interaction is by far the most important of the three. This assumption is not without basis. If one considers averages of the form $\langle r^{-p} \rangle$ to be approximately equal to a^{-p} where a is some reasonable atomic dimension, say $a \approx 10^{-9}$ cm, then one finds the electrostatic energy to be about 10^3 times as large as either

of the other two.[16] Therefore, in order to obtain the atomic state that has the least energy, it is proper first to minimize $E(\mathbf{r})$, and then to consider the other interactions only as they may be compatible with the results of such a minimization. The arguments that follow hinge on the validity of this statement.

Consider an atomic system of N equivalent electrons, each with l units of angular momentum. The electrostatic energy between two of these electrons is of the form $(|\mathbf{r}_1 - \mathbf{r}_2|)^{-1}$ so that the least energy is obtained when the probability (on the average) of finding the two electrons close to each other is smallest. It is a property of wavefunctions which are antisymmetric in the *spatial* coordinates of the electrons that the probability of finding any two of the electrons in the same infinitesimal volume is zero. (Of course, the total wavefunction for N electrons, including spin, must always be antisymmetric on the interchange of both the *spatial* and *spin* coordinates of any two electrons.) Thus, a plausible assumption is that the state with least energy will be of this type.[17] The antisymmetrization of the spatial part of the wavefunction involving N equivalent electrons is possible only when $N \leq 2l + 1$ (less than or equal to half a filled shell)[18] so that we phrase a postulate based on the observations stated above with this consideration in mind:

Postulate 1. The ground state wavefunction of a configuration involving N equivalent electrons is as maximally antisymmetric in the spatial coordinates of the electrons as is compatible with the exclusion principle.

Necessarily associated with an antisymmetric spatial wavefunction is a symmetric spin func-

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[13] On the basis of the discussion later in the paper, one would expect $J = L - S$ in this case, also. However, this configuration is attained in practice only for a highly excited atom, where the violation of Hund's rule is frequent and simple analysis is insufficient.

[14] J. Slater, Phys. Rev. **34**, 1293 (1929).

[15] See Ref. 4., p. 158.

[16] R. B. Leighton, *Principles of Modern Physics* (McGraw-Hill Book Company, Inc., New York, 1959), Sec. 8–2, p. 256; H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 181. These references give the interactions among atomic electrons.

[17] In J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952), p. 769, just the opposite argument is used for nucleons which find themselves in a net attractive potential in a nucleus, i.e., their spatial wavefunction tends to be symmetric on the interchange of nucleon coordinates.

[18] Antisymmetrization is tantamount to assigning each electron a unique set of quantum numbers. There are only three quantum numbers n, l, and m_l associated with the spatial functions, and since equivalent electrons may differ only in m_l, the number that can enter in such a state is limited by the number of possible values $(2l + 1)$ for m_l.

tion, in order that the product be totally anti-symmetric. If the number of equivalent electrons exceeds half a filled shell, then at most, the electrons in the first half-shell can be spatially antisymmetric (spin-wise symmetric) on interchanges among themselves, and similarly for those electrons in the second half-shell. The total wavefunction (including spin) must then be antisymmetrized on interchanges between the electrons occupying different half-shells. For the symmetric spin function, the following theorem applies:

Theorem 1. A necessary and sufficient condition that the total spin of p-spin one-half particles is the maximum possible, i.e., $\frac{1}{2}p$, is that the spin function for those particles is symmetric on the interchange of any two.

Proof. The proof of this theorem is simple if one utilizes the operator m_{ij} which interchanges the spin projections of the ith and jth particles.[19] For spin one-half particles, the product $\mathbf{s}_i \cdot \mathbf{s}_j$ is given by

$$\mathbf{s}_i \cdot \mathbf{s}_j = \tfrac{1}{2}(m_{ij} - \tfrac{1}{2} + \delta_{ij}), \qquad (1)$$

where $\mathbf{s}_i$ is the spin operator for the ith particle, δ_{ij} is the Kronecker delta, and the units are such that $\hbar = 1$. The simplest check that this relationship is valid is when $i = j$. Then it is known that $\mathbf{s}_i \cdot \mathbf{s}_i = \tfrac{1}{2}(\tfrac{1}{2} + 1) = \tfrac{3}{4}$. On the other hand, $m_{ii} = \delta_{ii} = 1$ so that the right hand side is also $\tfrac{3}{4}$.

(a) *Sufficiency Proof.* Assume χ_E is a symmetric spin function involving p-spin one-half particles. Then

$$\mathbf{S}^2\chi_E = (\sum_{ij} \mathbf{s}_i \cdot \mathbf{s}_j)\chi_E, \qquad (2)$$

where

$$\mathbf{S} = \sum_i \mathbf{s}_i. \qquad (3)$$

Using (1),

$$\mathbf{S}^2\chi_E = \sum_{ij} \tfrac{1}{2}(m_{ij} - \tfrac{1}{2} + \delta_{ij})\chi_E$$

$$= (\sum_{ij} \tfrac{1}{4} + \sum \tfrac{1}{2})\chi_E$$

$$= \tfrac{1}{2}p(\tfrac{1}{2}p + 1)\chi_E, \qquad (4)$$

since

$$m_{ij}\chi_E = \chi_E. \qquad (5)$$

(b) *Necessity Proof.* Assume that χ involves p-spin one-half particles and that

$$\mathbf{S}^2\chi = \tfrac{1}{2}p(\tfrac{1}{2}p + 1)\chi. \qquad (6)$$

Using (1), we obtain

$$(\sum_{ij} m_{ij})\chi = p^2\chi, \qquad (7)$$

or

$$\sum_{ij} \chi^+ m_{ij}\chi = p^2, \qquad (8)$$

assuming the normalization

$$\chi^+\chi = 1. \qquad (9)$$

In general, if the state χ is written as the sum of two terms, one even and the other odd on the interchange of particles i and j, it is readily shown that

$$\langle m_{ij} \rangle = \chi^+ m_{ij}\chi \leq 1, \qquad (10)$$

so that

$$\sum_{ij} \langle m_{ij} \rangle \leq p^2, \qquad (11)$$

with equality only in the event that $m_{ij}\chi = \chi$ for all i and j. But from (5), it is seen that the equality does hold, hence $\chi = \chi_E$.

On the basis of this theorem and the postulate stated previously, the primary requirement of Hund's rule, that is, maximum S, follows directly. If $N \leq 2l + 1$, the spatial (spin) wavefunction is antisymmetric (symmetric) and the spin of the lowest level is given by

$$S = \tfrac{1}{2}N. \qquad (12)$$

If $2l + 1 < N \leq 2(2l + 1)$, then the spatial (spin) wavefunction describing the electrons in each half-shell are antisymmetric (symmetric) on interchanges within the respective half-shells. Consequently, the spin S_1 for the $2l + 1$ electrons in the first half-shell, is $\tfrac{1}{2}(2l + 1)$, and the spin associated with the remaining electrons S_2 is $\tfrac{1}{2}[N - 2l - 1]$. The spins $\mathbf{S}_1$ and $\mathbf{S}_2$ are forced by the exclusion principle to be antiparallel[20] so that the spin for the system in this case is $S = S_1 - S_2$ or

$$S = \tfrac{1}{2}[2(2l + 1) - N] = \tfrac{1}{2}\tilde{N}, \qquad (13)$$

where $\tilde{N}$ is the number of "holes" in the shell.

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[19] This operator is used in nuclear theory and is attributed to Bartlett. Some of its more obvious properties are $m_{ij} = m_{ji}$; $(m_{ij})^2 = 1$; $m_{ii} = 1$ and $m_{ij}m_{jk} = m_{ki}m_{ij} = m_{jk}m_{ki}$.

[20] From the exclusion principle, the electrons in the second half-shell must possess m_s values differing from those in the first half-shell. Thus, if S_1 is oriented to have maximum z projection, i.e., $(S_{1z})_{max} = S_1$, each electron in this shell has $+\frac{1}{2}$ projection so that each electron in the second half-shell must have $-\frac{1}{2}$ projection.

It is, therefore, a consequence *merely of minimizing*[21] *the energy due to the electrostatic repulsion among the electrons* that the system tends to be in a state of maximum spin S. What is clear is that these results *do not owe their origin* to the spin–spin interactions that are known to exist in an atom!

The spin–orbit interaction, although limited to a degree by the foregoing considerations, can otherwise come into full play to further minimize the energy. This interaction is of the form $\zeta \sum \mathbf{s}_i \cdot \mathbf{l}_i$, where ζ is a positive quantity[22] so that minimum energy is obtained for antiparallel alignments of the spins with the orbital angular momenta. If the spins of the electrons are all in the same direction, then the $\mathbf{l}_i$ align *maximally* antiparallel to this direction. Thus, for $N < 2l+1$, the resultant orbital angular momentum L is antiparallel to S and has the magnitude[12]

$$L = \sum_{\nu=0}^{N-1} (l-\nu) = \tfrac{1}{2}N(2l+1-N). \qquad (14)$$

Since $\mathbf{L}$ and $\mathbf{S}$ are antiparallel, this suggests that the ground state has a definite total angular momentum given by $J = L - S$. In case $N = 2l+1$, then $\mathbf{L} = 0$ and $\mathbf{J} = \mathbf{S}$.

The situation for $2l+1 < N \leq 2(2l+1)$ can be similarly analyzed. The total orbital angular momentum results solely from the electrons in the second half-shell (for the closed half-shell $\mathbf{L}_1 = 0$) and is, accordingly, antiparallel to $\mathbf{S}_2$; however, the total spin for the system is determined by the direction of $\mathbf{S}_1$ since $S_1 \geq S_2$, thus $\mathbf{L}$ and $\mathbf{S}$ are parallel and $J = L + S$. In terms of $\tilde{N}$, we have in this case,

$$L = \tfrac{1}{2}\tilde{N}(2l+1-\tilde{N}). \qquad (15)$$

It is, therefore, a consequence of minimizing the spin–orbit interaction that the ground state has maximum L consistent with the requirements of minimum electrostatic energy, that is, consistent with maximum S. This is Hund's rule.

III. EXCITED LEVELS

As a demonstration of the usefulness of the simple notions set forth in the previous section,

let us consider the configuration nf^6, i.e., six equivalent electrons with $l = 3$. The ground state is expected to have $S = 3$, $L = 3$ and $J = L - S = 0$, and is designated $^7F_0$. Judd[23] gives a diagram of the energy levels of this configuration calculated on the basis of hydrogenic wavefunctions. Simply on the basis of the statement of Hund's rule, one would expect the group of excited states nearest to the ground state to be characterized by $S = 2$ (a relaxation of the primary requirement of Hund's rule), the next group by $S = 1$, and so forth. Among the states in each group, the state with maximum L would be expected to be lowest. For $S = 2$, five electrons have, say, spin projection $\tfrac{1}{2}$ and one electron has spin projection $-\tfrac{1}{2}$. Thus, the maximum L is the maximum for the five electrons $L_1 = 5$, plus the maximum for the one electron, $L_2 = 3$. That is, for $S = 2$, $L = L_1 + L_2 = 8$ is expected simply by a "rule of thumb" extension of Hund's rule. However, on the basis of the discussion in the previous section, it is clear that $\mathbf{L}_1$ and $\mathbf{L}_2$ are antiparallel for minimum spin–orbit energy (since the spins of the associated groups of electrons are antiparallel), and on this basis one would expect $L = L_1 - L_2 = 2$ to give the total orbital angular momentum of the lowest-lying state. The calculations based on hydrogenic wavefunctions agree with the latter prediction, i.e., the ^5D state is the lowest among the $S = 2$ states. Similarly, for $S = 1$ and $S = 0$, the analysis according to the previous section predicts lowest levels of ^3P and ^1S, respectively, again in agreement with the hydrogenic-wavefunction calculations.

IV. CONCLUSIONS

It has been shown that a consideration of the Coulombic and spin–orbit interactions between electrons of a given configuration is sufficient to arrive at a lowest energy state consistent with Hund's rule. It was argued that, to a first approximation, the spin–spin interaction is not a factor in determining the properties of this lowest state. The maximum-spin requirement is a result of considering the Coulombic interaction alone, whereas maximum L is a result of

[21] The word "minimizing" is used here in the context of the assumptions that were clearly stated previously. Of course no analytic minimization process has taken place.

[22] See Ref. 4, p. 122.

[23] B. R. Judd *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1962), p. 212, Figs. 8–3.

minimizing the spin–orbit energy which, in addition, provides the correct J value for configurations of equivalent electrons.

The interactions considered above do not exhaust all of the interactions that are present in an atom;[16] however, in most atomic systems, these are the most important and certainly are adequate to provide answers that are qualitatively correct in many cases. The understand-ing of the physical basis for Hund's rule has been shown here to be one such case.

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A Library of Experiments

FRANK OPPENHEIMER AND MALCOLM CORRELL
The University of Colorado, Boulder, Colorado
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A new concept in physics laboratory instruction is described in which the experiments are available to the student in much the same fashion as books in a library. The general nature of the experiments is explained and the philosophy underlying the use of the laboratory for instruction is discussed.

THE University of Colorado is developing a new concept of physics laboratory instruction for lower-division physics courses. We are constructing a "library of experiments" in which the apparatus for an experiment is nearly as accessible as are the books in the stacks of a university library. Our library at present contains about sixty-five different experiments, two-thirds of which have at least one duplicate. Eventually we hope to have between eighty and ninety different experiments.

These experiments are set up permanently on metal tables which can be moved from one location to another by means of a specially constructed dolly. The tables containing the experiments in most active use are located in a single large room whose area is about 3200 sq ft, while the remainder of the tables are stored in an adjacent room. The library-laboratory is open regularly from 8:30 a.m. to 9:00 p.m. and the scheduled laboratory classes meet in this room. Moreover, individual students are encouraged to return to perform experiments on their own. The laboratory sections are conducted by the regular teaching staff of the Physics Department, and a technician who is thoroughly familiar with the experiments is on hand during all open hours of the library.

Under this concept of laboratory instruction the students may be expected to do two or three experiments in the course of a 2-h period. In general, of course, students get more out of a laboratory session if the experiments have been discussed and if the procedures have been demonstrated during a previous session. Ways in which this may be handled are discussed below.

THE PEDAGOGICAL PURPOSE OF THE LABORATORY

The experiments in our library are not research projects and we make no pretense that the student is led to discover the laws of physics or even to establish them firmly. Moreover, since the setups are ready made for the student, we cannot claim that one of the objectives of the laboratory instruction is to teach laboratory technique by assembling apparatus for an experiment.

The experiments, however, are designed to be both *exercises and demonstrations* which are closely related to the content of the course. In

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